



Photocatalytic Activity of Rhodamine B using Alginate Supported Photocatalyst

V. Vidhya, A. Nithya, V. Kavin kumar K. Jothivenkatachalam*

Department of Chemistry, Anna University, BIT Campus, Tiruchirappalli, TN, India.

Received: 10.07.2018 Accepted: 14.08.2018

Abstract

Titanium dioxide-Alginate ($\text{TiO}_2\text{-Alg}$) and Zinc oxide-Alginate (ZnO-Alg) nanocomposites were synthesized, and their optical, structural, spectral and morphological analyses were carried out by several techniques. The prepared $\text{TiO}_2\text{-Alg}$ and ZnO-Alg nanocomposites act as a photocatalyst for the removal of Rhodamine B (RhB) dye under visible light irradiation. The pseudo-first-order kinetics was derived according to Langmuir-Hinshelwood (L-H) model.

Keywords: Photocatalytic Activity; ($\text{TiO}_2\text{-Alg}$); (ZnO-Alg); nanocomposites.

1. INTRODUCTION

Water is a very important compound present on the surface of the earth, and 71% of the earth's surface is covered by water. Unfortunately, due to the rapid increase in population and industrial activities, water demand and generation of wastewater start increasing. Wastewater from different sources, such as industry, municipal and agriculture, contain various types of contaminants. Industrial wastewaters usually possess organic and inorganic contaminants, such as phenolic compounds, dyes and heavy metals (Shannon *et al.* 2008). In recent years, water pollution has been increased greatly due to an increase in the toxic chemicals as reacting species from the industries and vast use of fertilizers in the agriculture sector. The dyes, phenolic compounds and heavy metals are highly toxic and produce carcinogenic, mutagenic and toxic problems to the human (Mangun *et al.* 2001; Pereira and Alves 2012; Geissen *et al.* 2015).

Moreover, the advanced oxidation processes like photocatalytic oxidation and reduction process are believed as an efficient technique for the removal of dyes and heavy metals from industrial effluent water without producing harmful by-products (Fu and Wang, 2011). The nanostructured semiconductors (SC) employing as a potential heterogeneous photocatalyst in the photocatalysis process. Moreover, the photo-functionalized nanostructured and nanocomposite materials can significantly improve their structural and catalytic properties. The semiconductor-metal nanocomposite materials have extensively investigated in photocatalytic organic and

inorganic pollutant degradation and received great advantages (Asmatulu *et al.* 2015; Yamashita and Li 2016). The semiconductor-biopolymer hybrid nanocomposite material has received huge attention in photocatalytic applications because of its interesting photonic, electronic and catalytic properties. The semiconductor-biopolymer nanocomposite materials have extensively investigated in photocatalytic and photoelectrocatalytic organic/inorganic pollutant degradation, methanol oxidation, photochemical conversion of carbon dioxide into hydrocarbon conversion, water splitting and solar photovoltaic applications (Arjunan *et al.* 2017; Karthikeyan *et al.* 2017). A great advantage has been observed to applying semiconductor-biopolymer nanocomposite material to photocatalytic and photoelectrocatalytic reaction process because of their large surface area, and high active sites are improved catalytic activity. Basically, nanomaterials physical, chemical and catalytic properties are mainly depending on their size and morphology of nanostructures (Tong *et al.* 2012).

In the present investigation, the biopolymer supported titanium dioxide and zinc oxide nanocomposite was synthesized and characterized. The prepared material photocatalytic activity was investigated for photocatalytic oxidation of rhodamine B under visible light irradiation and dark condition. This coupled effect was effectively decreased the charge recombination process and enhancing photocatalytic efficiency. The photocatalytic advanced oxidation process exists a

*Jothivenkatachalam

Email: kjothivenkatachalam@gmail.com

photofunctionalized semiconductor as photocatalyst for the photocatalytic oxidation process. The development of a cost-effective method has been suggested for the degradation of the dyes without producing any toxic products.

2. MATERIALS & METHODS

Chemicals

The materials required for the preparation, Titanium isopropoxide, zinc acetate ($\text{Zn}(\text{OAc})_2$), oxalic acid, were purchased from Merck Chemicals, India. And isopropanol, alginate (Alg) was purchased from Hi-Media, India. The rhodamine dye B ($\text{C}_{28}\text{H}_{31}\text{ClN}_2\text{O}_3$), was purchased from Merck Chemicals, India. All chemicals were used as received, without any further purification. The double-distilled water was used for all the experiments.

Preparation of Titanium dioxide-Alginate nanocomposites

In this process, 2 ml of titanium isopropoxide added with 50 ml of solvent (20 ml of isopropanol + 30 ml of distilled water) and stirring for 6 hrs. After 6hrs stirring continuously added 0.2 g of sodium

alginate which is dissolved in 20 ml of distilled water and leaving stirring for 6hrs further. Then obtained yellow precipitate was washed and centrifuged with distilled water and ethanol, then dried at 120 °C for 1 hrs and obtained TiO_2 -Alg nanocomposite.

Preparation of Zinc oxide-Alginate nanocomposites

In this process, 1.09 g of $\text{Zn}(\text{OAc})_2$ and 0.45 g $\text{C}_2\text{H}_2\text{O}_4$ was dissolved in 100 ml distilled water and stirring for 6 hrs. After 6hrs stirring, continuously added 0.2 g of sodium alginate, which is dissolved in 20 ml of distilled water and left stirring for 6hrs further. Then obtained white precipitate was washed and centrifuged with distilled water and ethanol, then dried at 120 °C for 1 hrs and obtained ZnO-Alg nanocomposite.

3. RESULTS AND DISCUSSION

UV- Diffuse Reflectance Spectra

The UV- Diffuse reflectance spectra (DRS) of TiO_2 -Alg and ZnO-Alg are shown in Fig. 1a and 1b. The samples show the clear UV absorption below 400 nm is resultant to excitonic absorption of TiO_2 -Alg and ZnO-Alg and the peak around 260-470 nm.

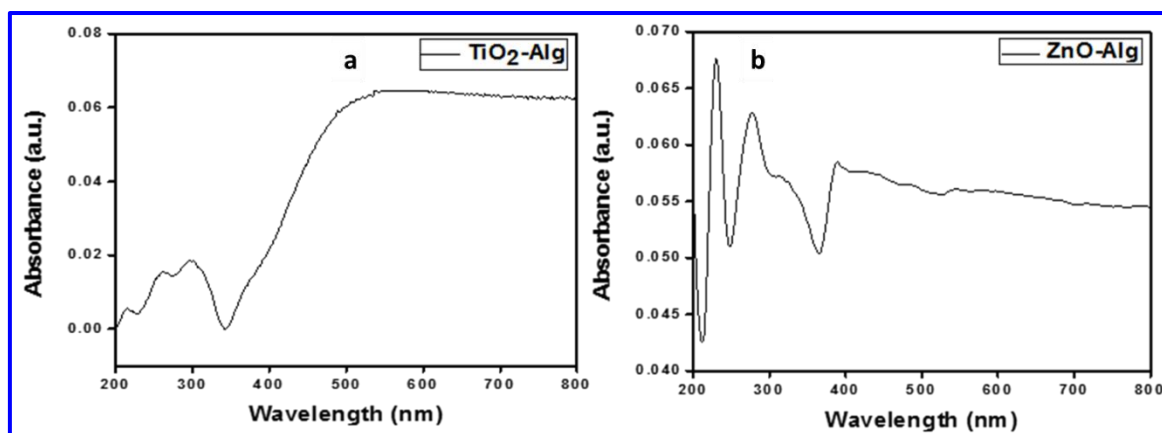


Fig. 1: UV-Diffuse reflectance spectra of (a) TiO_2 -Alg and (b) ZnO-Alg nanocomposites

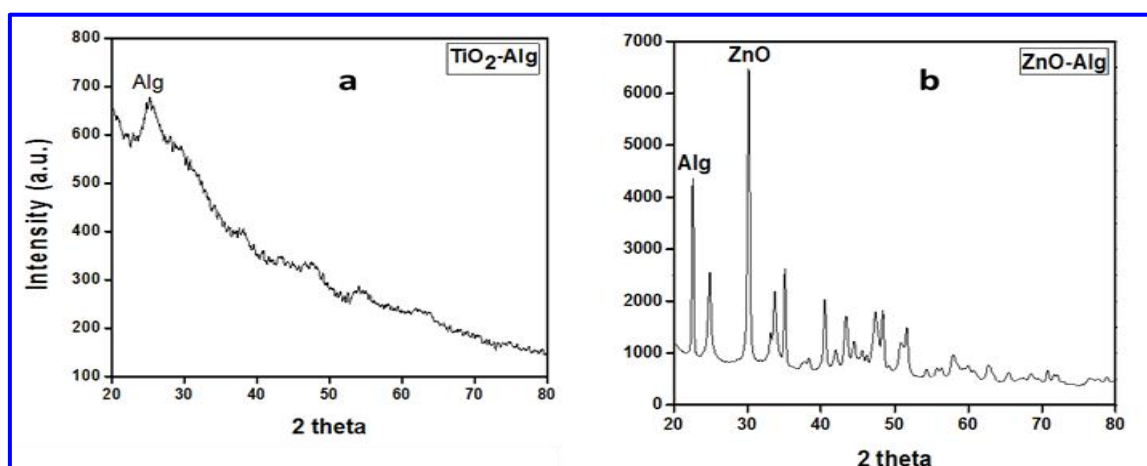


Fig. 2: XRD pattern of (a) TiO_2 -Alg and (b) ZnO-Alg nanocomposites

X-ray Diffraction Analysis

The XRD pattern of TiO_2 -Alg and ZnO-Alg nanocomposites were shown in Fig. 2. The lattice parameters were determined to be $a = 3.777$ for TiO_2 and $a = 3.249$ for ZnO that matches with the Joint Committee on Powder Diffraction Standards (JCPDS) file No. 89-4921 and No. 36-1451. There are no additional peaks in the spectra, indicating that there are no other impurities present in the nanocomposites (Nithya and Jothivenkatachalam 2014; Nithya et al. 2015).

FT-IR Analysis

FT-IR spectrum of TiO_2 -Alg and ZnO-Alg nanocomposite material are shown in Fig. 3 is given below. The FT-IR spectrum of alginate is differed from that of TiO_2 -Alg & ZnO-Alg composite, peak at around 3410 cm^{-1} due to stretching vibration of

hydroxyl and amino groups of alginate. The band at around 2130 cm^{-1} was due to stretching vibration of $-\text{CH}$ group, 1645 cm^{-1} indicated the amide group of C-O stretching, 1421 cm^{-1} showed the C-N axial deformation, 1388 cm^{-1} was due to COO group of carboxylic acid. The TiO_2 -Alg & ZnO-Alg composite displayed the characteristic bands of both ZnO and TiO_2 . The corresponding peaks are an indication of Ti-O, Zn-O immobilization onto the alginate.

Scanning Electron Microscope

The morphology and size of TiO_2 -Alg and ZnO-Alg nanocomposite material were analyzed by scanning electron microscope analysis is represented in Fig. 4. The result display that the TiO_2 -Alg particles are irregular in shape, and ZnO-Alg particles are spherical in shape presented over the polymeric alginate surface with aggregated structure.

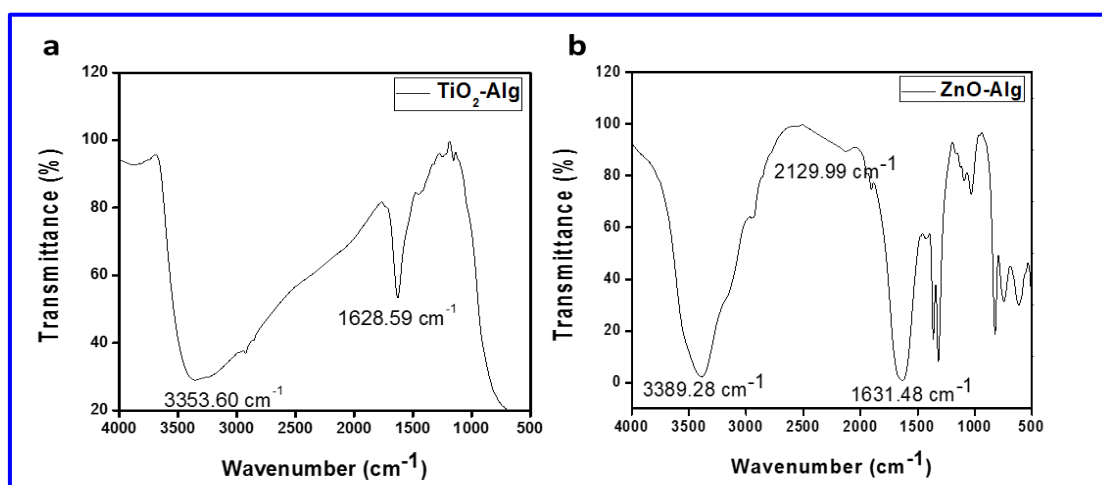


Fig. 3: FTIR spectra of (a) TiO_2 -Alg and (b) ZnO-Alg nanocomposites

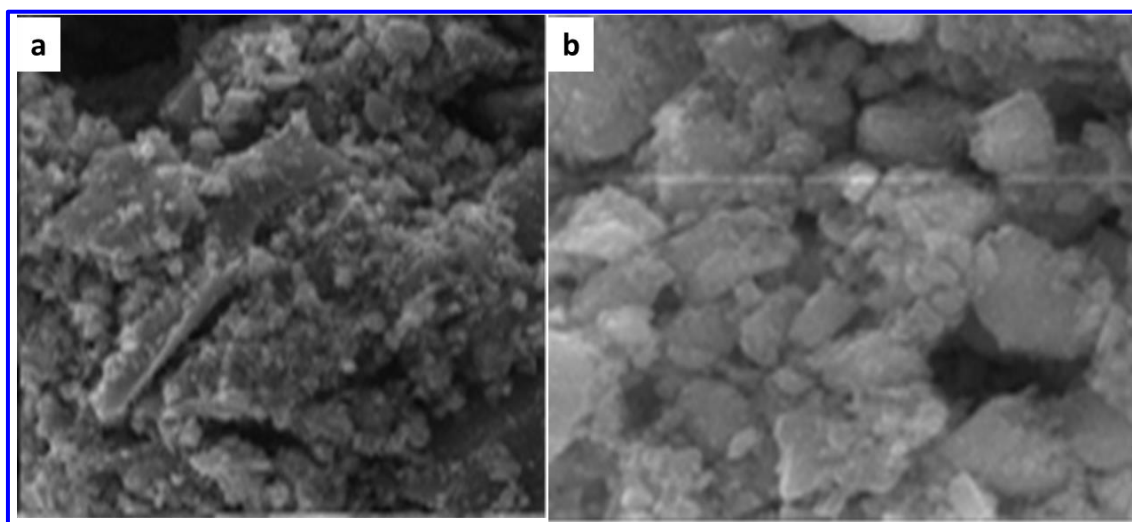


Fig. 4: FE-SEM image of (a) TiO₂-Alg and (b) ZnO-Alg nanocomposites

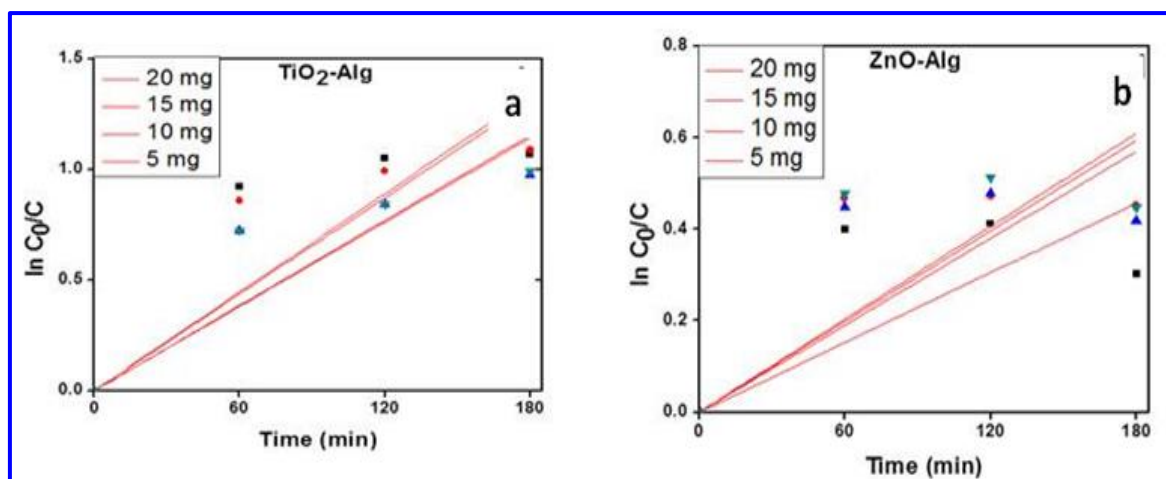


Fig. 5: Photocatalytic degradation of RhB in the presence of (a) TiO₂-Alg and (b) ZnO-Alg nanocomposite under visible light.

Photocatalytic degradation of Rhodamine B

The photocatalytic activity of the as-prepared TiO₂-Alg and ZnO-Alg were evaluated by photo-oxidation of rhodamine B (RhB) as a model organic pollutant under tungsten (~350-800 nm). The photocatalytic degradation was investigated by using 5 mg, 10 mg, 15 mg, 20 mg of TiO₂-Alg and ZnO-Alg was loaded into 5 ppm RhB aqueous solution at neutral pH. TiO₂-Alg nanocomposite achieved 60-70% degradation efficiency under visible light irradiation. It promotes electron-hole charge separation and reduces charge recombination rate.

4. CONCLUSION

TiO₂-Alg, ZnO-Alg nanocomposite materials were synthesized by precipitation and chemical reduction method. The prepared materials were characterized by UV-DRS, XRD, FTIR and HR-SEM analysis. The morphology analysis was displayed the TiO₂-Alg & ZnO-Alg are existed irregular and

spherical like morphology. The photocatalytic activities of the TiO₂-Alg & ZnO-Alg were successfully investigated by degradation of organic pollutant rhodamine B under visible light irradiation and dark condition. The degradation efficiency TiO₂-Alg nanocomposite was increased compared to ZnO-Alg. The synergetic effect of alginate promoting electron-hole charge separation and transfer process belongs to increase the active radical, photocatalytic reduction and oxidation process. Hence, TiO₂-Alg nanocomposite showed an efficient photocatalytic activity for the degradation of organic pollutant.

REFERENCES

- Arjunan, N., Singaravelu, C. M., Kulanthaivel, J., Kandasamy, J., A potential photocatalytic, antimicrobial and anticancer activity of chitosan-copper nanocomposite, *Int. J. Biol. Macromol.* 104, 1774–1782 (2017).
doi: 10.1016/j.ijbiomac.2017.03.006

- Asmatulu, R., Nuraje, N., Mul, G., Chapter 1. Introduction to Green Nanostructured Photocatalysts, *Royal Society of Chemistry*, 01–12(2015).
[doi:10.1039/9781782622642-00001](https://doi.org/10.1039/9781782622642-00001)
- Fu, F. and Wang, Q., Removal of heavy metal ions from wastewaters: A review, *J. Environ. Manage.* 92(3), 407–418 (2011).
[doi: 10.1016/j.jenvman.2010.11.011](https://doi.org/10.1016/j.jenvman.2010.11.011)
- Geissen, V., Mol, H., Klumpp, E., Umlauf, G., Nadal, M., van der Ploeg, M., van de Zee, S. E. A. T. M., Ritsema, C. J., Emerging pollutants in the environment: A challenge for water resource management, *Int. Soil Water Conserv. Res.* 3(1), 57–65 (2015).
[doi: 10.1016/j.iswcr.2015.03.002](https://doi.org/10.1016/j.iswcr.2015.03.002)
- Karthikeyan, K. T., Nithya, A., Jothivenkatachalam, K., Photocatalytic and antimicrobial activities of chitosan-TiO₂ nanocomposite, *Int. J. Biol. Macromol.* 104, 1762–1773 (2017).
[doi: 10.1016/j.ijbiomac.2017.03.121](https://doi.org/10.1016/j.ijbiomac.2017.03.121)
- Mangun, C. L., Yue, Z., Economy, J., Maloney, S., Kemme, P., Cropek, D., Adsorption of Organic Contaminants from Water Using Tailored ACFs, *Chem. Mater.* 13(7), 2356–2360 (2001).
[doi: 10.1021/cm000880g](https://doi.org/10.1021/cm000880g)
- Nithya, A., JeevaKumari, H. L., Rokesh, K., Ruckmani, K., Jeganathan, K., Jothivenkatachalam, K., A versatile effect of chitosan-silver nanocomposite for surface plasmonic photocatalytic and antibacterial activity, *J. Photochem. Photobiol. B Biol.* 153, 412–422 (2015).
[doi: 10.1016/j.jphotobiol.2015.10.020](https://doi.org/10.1016/j.jphotobiol.2015.10.020)
- Nithya, A., Jothivenkatachalam, K., Visible light assisted TiO₂- chitosan composite for removal of reactive dye, *J. Environ. Nanotechnol.* 3(3), 20–26 (2014).
[doi: 10.13074/jent.2014.09.42085](https://doi.org/10.13074/jent.2014.09.42085)
- Pereira, L., Alves, M., Dyes—Environmental Impact and Remediation, In: *Environmental Protection Strategies for Sustainable Development*. Springer Netherlands, Dordrecht, 111–162(2012).
- Shannon, M. A., Bohn, P. W., Elimelech, M., Georgiadis, J. G., Mariñas, B. J. and Mayes, A. M., Science and technology for water purification in the coming decades, *Nature* 452(7185), 301–310 (2008).
[doi: 10.1038/nature06599](https://doi.org/10.1038/nature06599)
- Tong, H., Ouyang, S., Bi, Y., Umezawa, N., Oshikiri, M., Ye, J., Nano-photocatalytic Materials: Possibilities and Challenges, *Adv. Mater.* 24(2), 229–251 (2012).
[doi: 10.1002/adma.201102752](https://doi.org/10.1002/adma.201102752)
- Yamashita, H., Li, H. (eds), *Nanostructured Photocatalysts*. Springer International Publishing, Cham.